Laboratory Investigation of the Potential for Re-emission of Atmospherically Derived Hg from Soils

M E I   X I N ,   M A E   G U S T I N ,*   A N D
D A L E   J O H N S O N

*Department of Natural Resources and Environmental Science,
University of Nevada, Reno, 1664 North Virginia Street, Reno,
Nevada 89557*

This paper presents data from controlled laboratory experiments focused on investigating the effect of moisture and visible and ultraviolet light on the emission and re-emission of mercury (Hg) from two soils, one with low or background Hg concentrations (14 ng g^{-1}) and a soil naturally enriched in Hg (4800 ng g^{-1}). Water addition was found to increase emissions from dry soils by an amount greater than that occurring during exposure to PAR or UV-A radiation, whereas UV-B and UV-C exposures facilitated the greatest release. Over all exposures, only a small percentage of Hg(II) added in a wet spike simulating a precipitation input was released immediately after addition (<3%). The majority of the Hg being released during all exposures was indigenous and either an original component of the soil or derived from past wet and dry deposition. Under dark and light conditions, elemental Hg was deposited to the dry low Hg-containing soil. On the basis of experimental results, it is hypothesized that dry deposition of gaseous elemental Hg is an important input to low Hg soils and that light, water, and UV-A exposure promote desorption and re-emission of elemental Hg. UV-B exposure is hypothesized to promote indirect photoreduction of Hg-(II) existing in the soil. The available pool and the form of Hg in the soil, as well as the chemistry of the soil, will determine the overall flux response to environmental stimulation of emissions.

Introduction

Air–soil exchange is an important component of the mercury (Hg) biogeochemical cycle (*1–3*). Factors shown to be important in influencing the magnitude of Hg release from soils are Hg concentration (*4, 5*), soil moisture (*6–8*) atmosphere oxidants (*9*), meteorological conditions (barometric pressure, temperature, wind speed and turbulence, and solar radiation) (*2, 3, 10–14*), and vegetative cover (*15*).

Mercury ccurrs naturally at low concentrations in most lithologic materials and can be added to terrestrial surfaces from the atmosphere by wet and dry process (*16*). Differentiation between emission of Hg pre-existing in the soil (geogenic) or that accumulated from historical wet and dry deposition is important for predicting Hg cycling, fate in ecosystems, and the effectiveness of actions to minimize sources of Hg to the atmosphere (*12, 17*).

* Corresponding author phone: (775)784-4203; fax: (775)784-4789; e-mail: mgustin@cabnr.unr.edu.

Mercury in the atmosphere occurs as elemental mercury (Hg°) and reactive gaseous (RGM), organic, and particulate forms. Elemental Hg, the dominant (95%) form in the atmosphere (*18, 1*), may be directly deposited to soil from the atmosphere (*3, 19–21*), whereas RGM and particulate Hg can be deposited by wet and dry processes (*1*). Recent work has suggested that monomethyl Hg may be formed in the atmosphere through a reaction with labile Hg(II) complexes and atmospheric methylating agents such as acetate (*22*).

Once deposited, Hg(II) forms may be reduced to Hg° and re-emitted to the atmosphere or it may become bound to constituents of the soil (*13*). The reduction of Hg(II) to Hg° can take place abiotically or biotically (*2*). The abiotic reduction of Hg(II) to Hg° has been shown to be enhanced by sunlight in the presence of organic acids and Fe oxides in solution (*2, 23–25*).

Several studies have investigated the effect of ultraviolet (UV) light on Hg emission from soils using filters (*3, 26*). Zhang et al. (*3*) in limited field experiments showed that reduction of UV and photosynthetically active radiation (PAR) reduced Hg emissions from soils. Moore and Carpi (*26*) applied specific filters to determine the influence of UV-A on Hg emissions using wet soils. They suggested that UV-A facilitated reduction of Hg(II), whereas increased temperature promoted Hg° release. They showed that the intensity of the exposure influenced the release. Here, we expand on these studies by investigating the impact of UV-A, -B, and -C radiation and PAR on Hg emissions from dry and wet soils.

Investigation of the potential for re-emission of Hg deposited to soils in precipitation has been done in only a few field studies using the addition of a concentrated Hg stable isotope spike (*17, 27, 28*). In general, data suggested that only a small component (<10%) of the added Hg (II) would be re-emitted over a year. An additional objective of this study was to conduct a series of experiments that would allow us to understand the combined effects of soil moisture and light on the immediate re-emission of Hg wet deposited versus their influence on the emission of Hg already present in the soil (indigenous). The working hypothesis was that external stimuli shown to enhance Hg emissions from soils would facilitate immediate re-emission of Hg that had been deposited to soils as HgCl$_2$ in precipitation.

Materials and Methods

One soil with natural background concentrations (14 ng g^{-1}) and a natural soil with elevated Hg concentrations (4800 ng g^{-1}) with respect to natural background Hg concentrations (<100 ng g^{-1}) (*29*) were used in this study (Table 1). Both soils were homogenized and sieved to <2 mm before use. The soil with the higher Hg concentration was collected from an area of precious metal mineralization and Hg enrichment in Nevada. The exact speciation of Hg in these soils is not known; however, it is generally assumed that Hg in soil is Hg(II) bound to organic materials and sulfur- or iron-containing phases (*30*).

Mercury flux was measured using a single-pass gas-exchange system that consisted of a continuously mixed Pyrex chamber with a volume of 12 L. Incoming air was cleaned of oxidants and Hg (Aadco Pure Air Generator) and a controlled amount of Hg° was added using a permeation tube within a Kintec Trace Gas Generator. Air flow through the chamber was controlled by a mass flow controller (Sierra Instruments) at 4 L min^{-1}. A Tekran 2537A Hg analyzer and a solenoid switching unit were used to measure air Hg°
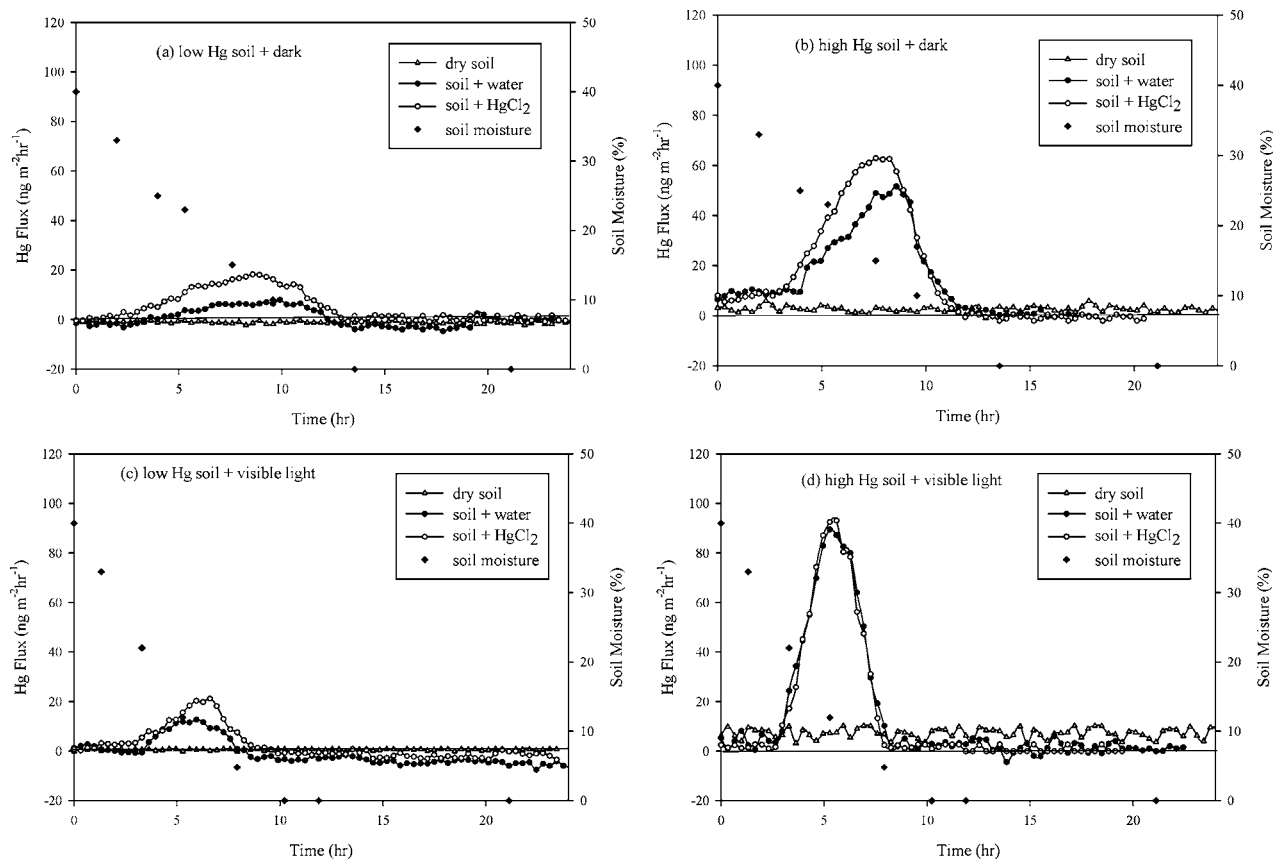
FIGURE 1. Hg° flux and soil moisture as function of time measured during dark and visible-light exposure.

TABLE 1. Characteristics of the Soils Used in This Study

soil type	field site location	soil type	Hg (ng/g)	particle size distribution (%)			OM (%)	pH	CEC (mequiv/100 g)	Mn (μg/g)	Fe (μg/g)
				sand	silt	clay					
low Hg soil	Norman, OK	mollisol	14	68	18	14	1.4	5.8	9.1	6	41
high Hg soil	Washington Hill, NV	mixture of aridisol and mollisol	4800	44	30	26	3.1	6.3	13.3	12	8

concentrations at the inlet and outlet of the chamber in two 5-min intervals (*10, 11*).

All Hg flux measurements were conducted at air Hg° concentrations of 2.1 ± 0.4 ng m^{-3} that is within the range of those reported for remote sites (*31*) at 27 ± 1 °C. Each exposure was done using a new 30 g aliquot of soil that was evenly distributed in a Petri dish (90 mm diameter). For wetting, either 20 mL of 18 MΩ high purity water (Millipore Milli-Q system; Hg < 1 ng L^{-1}; pH 7) or 20 mL of a high-purity water plus HgCl$_2$ solution (Hg concentration: 2.7 ± 0.3 μg L^{-1}, pH 5.5) was added to saturate the soil. The soil was then allowed to dry in the chamber for 24 h, during which continuous 20 min fluxes were measured. The applied amount of HgCl$_2$ was equivalent to a wet deposition amount of 10 μg m^{-2}, which is higher than the annual wet deposition for Nevada (*32*) and lower than that reported for the eastern area of United States (*33*). Soil moisture concentrations were determined for each exposure scenario gravimetrically in regular time intervals. Soils dried most rapidly in the visible light conditions, and the water loss over time for the dark and UV exposures were similar (Figures 1 and 2).

One experiment was done to investigate the potential for Hg° uptake using 100 g of dry low Hg soil in a 140 mm diameter Petri dish exposed to cleaned air with concentrations ranging from 0 to 200 ng m^{-3} at 25 °C in the dark.

Exposure time for each concentration varied from 2 to 17 h (Figure 3). This experiment was replicated and the same results were obtained. The empty chamber flux was determined for each experimental Hg° exposure condition, and all resulting flux data were corrected using the following linear relationship to calculate deposition ($C_{inlet} - C_{outlet} = C_{inlet^-}$ (0.012 ± 0.002) − 0.29 ± 0.2). A chamber blank of 0.38 ng m^{-2} h^{-1} was applied to all other data on the basis of blank measurements between experiments.

Two different light sources were used in this study. A spot light (QBEAM Brinkmann Corporation) provided PAR in the chamber with an intensity of 250 W m^{-2} (Li-Cor LI200X) and a UV light source (UVP model 3UV-34 with manufacturer provided wavelengths and light intensities) with three UV tubes (UV-A, 365 nm 1.147 W m^{-2}; UV-B, 302 nm 0.778 W m^{-2}; and UV-C, 254 nm 1.070 W m^{-2}). Light sources were situated outside and inside the glass chamber, respectively. For comparison, mean PAR in Reno in the winter is similar to the exposure used in this study, whereas UV-B radiation ranges from 0.41 to 2.23 W m^{-2} for a solar zenith angle of 0 to 60°, respectively, and UV-A from 27 to 66.5 W m^{-2} (*34*). The ratio of PAR to UV radiation is ~84.5:16.5, with UV-A constituting most (>90%) of the UV component (*34, 35*). Thus, UV-A exposures were low relative to natural radiation;
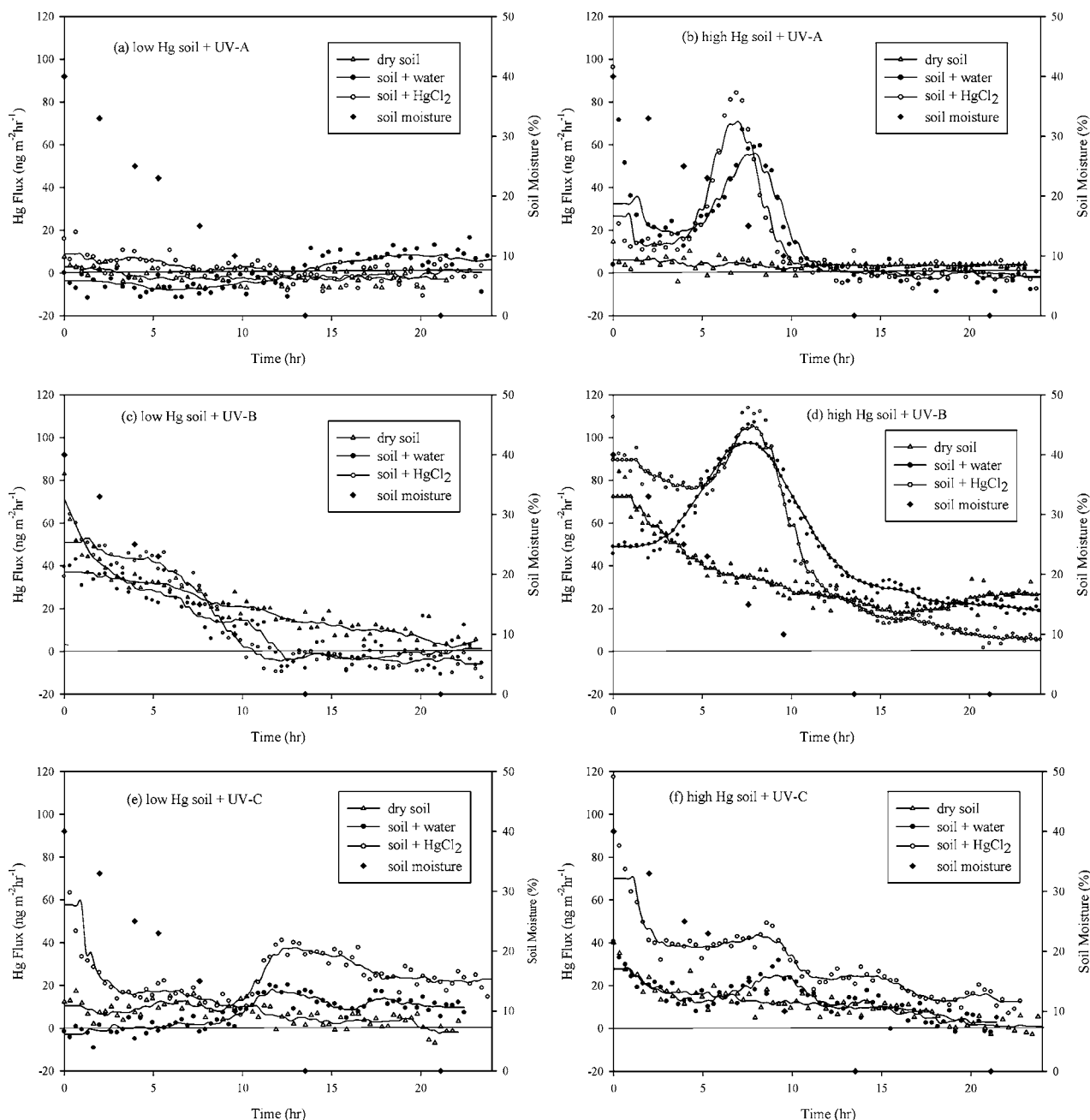
FIGURE 2. Hg° flux and soil moisture as a function of time measured during UV-light exposures.

however, UV-B and PAR were within the range of natural inputs.

Statistical tests were run using Minitab (version 12) with significance at $p < 0.05$. A running average with a sample proportion of 10% was used to make the smoothed flux curves, allowing for calculation of cumulative flux for each 24 h experiment using the trapezoidal rule. The amount of Hg emitted from the soil that could be the $HgCl_2$ amended in the solution spike was determined using the following equation

Hg(II) re-emitted (%) =
$$\frac{\text{total Hg loss, } HgCl_2 \text{ (ng)} - \text{total Hg loss, water (ng)}}{\text{total Hg, } HgCl_2 \text{ (ng)}} \times$$
$$100\% \quad (1)$$

where total Hg loss was calculated on the basis of the 24 h data shown in Figures 1 and 2, and the total Hg applied was 55 ± 5 ng. This assumes that the Hg released from the soil

saturated with ultraclean water was that pre-existing in the soil prior to the experiment (total Hg in 20 mL ultraclean water was ~0.02 ng), whereas the emissions from the soil amended with $HgCl_2$ solution included a component similar in magnitude to that of the water amended soil plus the re-emission of the Hg(II) added in $HgCl_2$ solution.

Results and Discussion

Dark and PAR Exposures. Samples of the dry low-Hg-containing soil adsorbed Hg from atmosphere (flux < 0) under both dark and PAR exposures, with deposition being higher in the dark (-2.2 ± 1.0 versus -0.6 ± 0.6 ng m^{-2} h^{-1}, respectively). The dry Hg-enriched soil emitted Hg to the atmosphere with visible light enhancing Hg release relative to dark conditions (7.3 ± 1.7 versus 2.4 ± 1.3 ng m^{-2} h^{-1}, respectively; Figure 1). Mercury fluxes in the dark from both the enriched and low-Hg-containing soil when the soils were first wetted with both solutions were low and increased as the soil dried with peak emissions occurring ~9 h after the
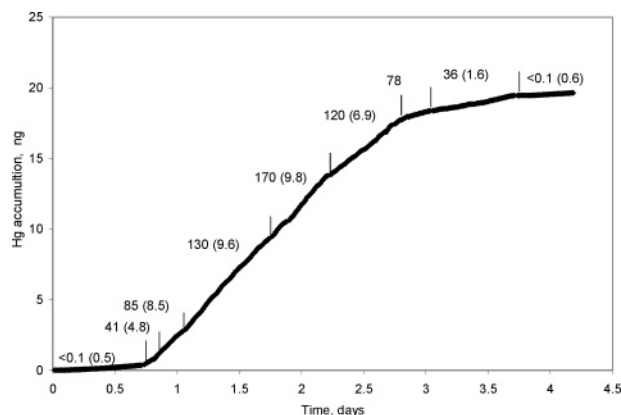
FIGURE 3. Hg° accumulation by soil over a range of air exposures at 25 ± 1 °C in the dark. Numbers indicates the air Hg exposure for that time of exposure, whereas the number in parentheses indicates the slope for the line on the basis of the data shown in the block.

water or $HgCl_2$ solution was added at a soil moisture of 12–15%. As the soil continued to dry, Hg flux then declined to values comparable to those measured from dry soil. This pattern of Hg release from saturated soils as they dry has been described in other studies (6–8). For both soils, emission in the dark after the $HgCl_2$ exposures were greater than that occurring from the soil with pure water added ($t = 11.17$, $p < 0.001$; $t = -2.26$, $p = 0.028$; respectively).

The flux versus time curves obtained for both soils exposed to PAR (panels c and d of Figure 1) were similar to that observed under dark conditions except for narrower peaks. This was most likely a response to faster drying during light exposures (7). For both soils when wet, similar amounts of Hg were released during the 24 h dark and PAR exposures and emissions were significantly greater than flux for dry soil (Table 2). This indicates that water has a more significant influence on Hg emissions than PAR at the exposures used. This may be due to the fact that water may enhance Hg release from within the soil profile depending on the depth of penetration, whereas light energy will have the greatest impact at the immediate surface (upper 2 mm) (36).

In the dark for 24 h, ~1.8 ng of Hg° was added by way of dry deposition to the low Hg soil, and in the light, 0.2 ng was added; the total Hg° emitted after the addition of water and $HgCl_2$ solution was 0.3 and 0.6 ng, respectively. Assuming 12 h of dark and light conditions for a dry soil, 1 ng could be added to the soil from the air over 24 h, which is greater than that emitted for the same time after wetting.

UV Exposures. Both soils when dry and exposed to UV-A exhibited steady fluxes similar in magnitude to that observed in the dark (both t-test: $p > 0.05$) implying that the UV-A exposure did not significantly influence Hg emission from dry soils (Figure 2). The pattern in flux after watering for the UV-A exposures was different than that observed during the dark and PAR exposures with higher Hg release from the $HgCl_2$ amended soils initially. However, the total amounts of Hg released during the dark, PAR, and UV-A exposures when wet were relatively the same (Figure 2; Table 2). Because UV-A intensity may influence the amount of Hg released (26), it is possible that more Hg would be emitted at higher UV-A intensity than used in this study.

During UV-B exposure, both soils when dry and wet exhibited initially significantly greater Hg emissions than that observed under dark, PAR, and UV-A exposures and fluxes gradually declined over time (panels c and d of Figure 2). After ~22 h, Hg emissions from the wet low-Hg-containing soil were similar in magnitude to those measured in the dark exposures. However, fluxes measured from the enriched soil

were higher than those measured during dark, PAR, and UV-A exposure after 24 h. The total amount of Hg released during 24 h from the UV-B exposures was significantly greater than that measured during the UV-A, PAR, and dark exposures for both soils. On the basis of these observations, we hypothesize that UV-A and PAR exposures, as well as the addition of water, facilitate the release of Hg° that was adsorbed to soil particles, whereas UVB promotes production of Hg° via photoreduction of Hg (II). Indirect photoreduction in the soil could occur via sunlight induced reactions with Fe-, Mn-, and organic-containing compounds in the soil, as has been shown to occur in solution (37). It is noteworthy that iron concentration of the low-Hg soil was significantly greater than the elevated-Hg-containing soil (Table 2) and the initial flux during UV-B light exposure was 50 times that observed for the UV-A, PAR, and dark exposures for the low-Hg-containing soil, and only 6-fold higher for the high Hg soil. Photochemical reactions would be limited by the Hg available in the surface (36), and this would explain the decline in flux with time.

The flux curves for the UV-B-exposed low-Hg soil under all three conditions followed the same trend over time, and no significant difference in emissions was observed between the water and $HgCl_2$ amended samples ($p > 0.05$; Figure 2). This indicates that photoreduction, if occurring, was not associated with the amended $HgCl_2$ but with Hg already existing within the soil. For the high-Hg soil, a higher release initially was observed for the dry and $HgCl_2$-amended soil relative to the wetted soil.

For both soils during UV-C exposure, emissions were highest from soils amended with $HgCl_2$ (both $p < 0.05$). The total amount of Hg released from the low-Hg-containing soil exposed to UV-C was higher than the amount released during exposure to UV-B (Table 2); however, this was not the case for the Hg-enriched soil. This may indicate that the speciation of Hg or chemistry of the soils could be influencing release. The wavelength of UV-C was close to that for Hg adsorption (253.7 nm) and may explain the greater influence of this light source on the release of newly added $HgCl_2$.

Soil Hg° Uptake. One limited experiment investigated the potential for Hg° adsorption and release by soils for ~5 days of initially increasing (~0–170 ng/m3) and then decreasing exposure concentrations. Although input concentrations as well as the time for the exposures varied, the soil adsorbed Hg° continuously (Figure 3). At high exposures, the uptake was fairly constant; however, as air concentrations were decreased, adsorption decreased (on the basis of the slope of the line in Figure 3) indicating some hysteresis. Although these exposures were high, this indicates that this low-Hg soil had a high adsorption capacity for gaseous Hg°. Others (38, 39) have studied Hg sorption by soils using high air exposures ($\mu g\ m^{-3}$) and found that the sorption increased with increasing Hg° concentrations. The data show that gaseous Hg uptake by soils does not follow the typical Langmuir Isotherm in that adsorption is not concentration dependent but rather seems to occur at a relatively constant rate once a (low) threshold concentration is reached. This suggests that adsorbed Hg is not remaining on the surface, as the Langmuir equation assumes, but rather is being incorporated into the soil by some process, and that process is controlled by something other than Hg concentrations in the input air.

Mercury Emission and Re-emission. The influence of PAR, UV-A, and UV-B on amended Hg(II) re-emission was small (<1%) and UV-C promoted release of ~3% of the $HgCl_2$ added (Table 2). The data indicated that all exposure scenarios enhanced emission of indigenous Hg from dry and wet soils over 24 h (Table 2); however, the percent released with respect to the total Hg pool in the soil was small (0.06% of that in the low Hg soil and much less for the enriched soil).

TABLE 2. Cummulative Hg° (ng) Flux for 24 h for Each Exposure Scenario (percentage of Hg (II) re-emitted on the basis of the amount added (55 ng))

	low Hg soil				high Hg soil			
	total Hg loss (ng)				total Hg loss (ng)			
	dry	+water	+HgCl$_2$	Hg (II) re-emitted (%)	dry	+water	+HgCl$_2$	Hg(II) re-emitted (%)
dark	−1.8	0.3 0.4[a]	0.6 0.5[a]	0.6 0.6[a]	0.5	1.6	1.9	0.6
visible light	−0.2	0.3 0.3[a]	0.5 0.6[a]	0.4 0.5[a]	1.1	1.7	1.7	0.0
UV-A	0.1	0.4	0.4	0.0	0.7	2.2	2.1	0.0
UV-B	1.6	1.8	2.1	0.5	5.3	7.3	7.6 7.2[a]	0.7
UV-C	0.9	2.5 2.8[a]	4.0 3.9[a]	2.7	1.8 1.7[a]	2.7 2.0[a]	4.5	3.3

[a] Replicate results.

Over 24 h, the amount of indigenous Hg released during exposure to water, PAR, and UV-A were similar, and significantly less than that measured during UV-B and UV-C exposures for both dry and wet soils. This suggests that two different pools of Hg in the soil were being exploited. We hypothesize that water, PAR, and UV-A exposures facilitated release of Hg°, whereas UV-B and UV-C resulted in conversion of Hg(II) to Hg° in the soil increasing the pool available for volatilization. Indigenous Hg in the soil could be a natural component or that input by way of dry and wet deposition that was sequestered in the soil. For example, although the spike of HgCl$_2$ in solution increased the low soil Hg concentration by ∼9%, only a small percentage of this spike (0.5−3%) was immediately re-emitted. Similarly, deposition of atmospheric Hg° to the low-Hg soil resulted in an addition of Hg that was greater than that released during 24 h after wetting. This study and others have also shown that atmospheric Hg° can be accumulated by soils. Adsorbed Hg° could be re-emitted with wetting and PAR exposures (as well as changes in temperature), facilitating release; UV-B exposures could eventually reduce Hg(II) added in precipitation events, making it available for volatilization. Perhaps Hg(II) deposited by wet processes needs to "mature" in the soil or become associated with components that would participate in photoreduction reactions before being impacted by UV-B.

Our results, indicating that HgCl$_2$ in solution was not released immediately after deposition (despite the fact the experiments were done in the laboratory at a small scale with air cleaned of ambient impurities with only two soils) are similar to those reported in field studies in which substrates were spiked with a HgCl$_2$ solution containing a specific stable isotope of Hg (17, 27, 28). For example, Ericksen et al. (17) reported that 0.1% of the Hg was released initially and only 2−3% of the stable isotope added released over the next 180 days. Thus, our working hypothesis was rejected in that Hg(II) added to simulate precipitation was not released immediately from soils; however, it appears that Hg deposited to soils by dry and wet processes may be gradually released over time in response to different environmental stimuli. This suggests that source reduction is important for mitigating future Hg availability.

Acknowledgments

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